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THE DETERMINATION OF SURFACE-TENSION

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This investigation is part of a series of investigations having for their object the study of the fundamental properties of liquids. It is hoped that, when a number of these properties have been determined with great accuracy, the essential relations between them may be discovered with greater certainty than is possible at present.

Among the significant properties of liquids surface-tension stands out as one of the most interesting. This somewhat unfortunately named property affords us a valuable clue concerning the cohesive forces which bind the substance together and cause it to become a liquid. Therefore, its exact determination is a matter of far-reaching importance to anyone who seeks to understand the fundamental nature of the liquid state.

A glance at the published data concerning surface-tension leads one to conclude that much remains to be done. For example, the values obtained by experienced men for water at 20° vary all the way from 70.6 to 78, according to different methods. Even a single method (for example, that of the rise in capillary tubes) has yielded results in the last twenty-five years varying from 70.6 to 72.7, and no satisfactory evidence is forthcoming as to the reasons for the difference.

It seemed therefore worth while not only to study the surface-tension of a variety of new liquids, but also to discover the reason for the divergences between different methods, and to obtain results of absolute as well as of relative accuracy for liquids already studied. The present work, although only preliminary, seems to have been successful in locating several of the heretofore not adequately heeded sources of error.

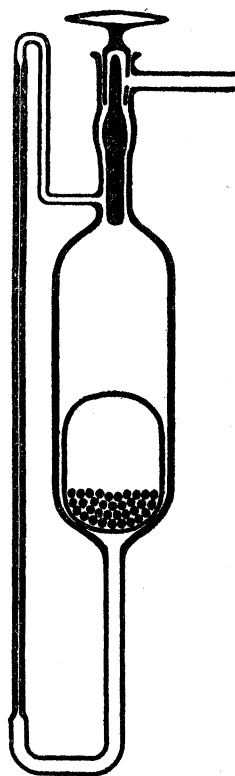
The method chosen was the well known method of capillary rise in carefully measured tubes, because this method seems to be one of the most direct and least likely to lead to insoluble mathematical complications. The method has been used by many experimenters in the past.

Several features of the present work deserve emphasis. In the first place, the careful selection of the capillary tubes and the calibration by means of short columns of mercury received especial attention. Correction was made for the menisci of these columns in determining the exact diameter of the tube. Again, great care was taken to determine exactly the position of the menisci, both of the larger and of the smaller surface, by means of a finely adjustable black screen behind the tubes to be measured. It was found that the exact position was

only to be observed when the meniscus appeared to be precisely tangent to the edge of the screen.

Both of these precautions have been more or less fully heeded by others; but another precaution, the determination of the diameter necessary for the larger tube in order to secure perfectly flat surface, has been often overlooked. We found that a tube over 35 mm. in diameter was required, and that even into this wide tube it was not permissible to insert a capillary; for such an insertion acted as another basis of support for the liquid and caused appreciable rise. By actual measurement we found that the capillary rise in a 20 mm. tube, counting only from the middle of the bottom of the meniscus, was over 0.5 mm., and the addition of a capillary tube in the middle of this raised it at least 0.3 mm. more. As apparatus of this sort has been used by most experimenters on surface-tension, most of the capillary rises which have been reported are in the neighborhood of 1 mm. too low—an error which accounts for a large part of the discrepancies between different methods.

Another error which does not seem to have received sufficient attention is that due to the weight of the liquid in the finer meniscus above its lowest point. The equation of Poisson, which is usually used for calculating this weight, gives an absurd result with tubes as wide as 1 cm., and therefore must be rejected. Another equation, that of Desains, gives a result for fine tubes which is not plausible; hence this also seemed unworthy of confidence. A careful measure of the height of the meniscus between its lowest point and its line of contact with the fully wetted walls showed that in very fine tubes this height is almost exactly equal to the radius, and that, therefore, the meniscus is here essentially hemispherical. As the tube widens, the hemisphere becomes somewhat flattened, and for moderate radii it appears entirely safe to apply, as a correction to be added on account of the meniscus, one-third of the meniscus height as actually measured. This method of correction was shown to give consistent results with tubes of different diameters.



APPARATUS IN DIAGRAMMATIC SECTION. (THE LOADED SINKER IS TO DIMINISH THE NECESSARY VOLUME OF LIQUID.)

Great difficulty and considerable liability for error were found in the inequalities of the glass of the tubes to be measured. Accordingly all measurements were made in reversible apparatus of the type shown in the diagram. This form of apparatus when exactly half filled with liquid is observed, first in an upright position in front and behind, and again in an inverted position in front and behind. Thus from the average, all the displacements due to refraction of irregular walls of the larger tube are entirely eliminated. The regularity of the walls of the smaller tube are tested by the calibration in the first place.

The preliminary results thus obtained are recorded in the table given below. All the measurements were made in the presence of air. The surface-tensions are calculated according to the well known equation $\gamma = \frac{1}{2} rhg (s_1 - s_2)$ in which the angle of contact of the meniscus in the tube is assumed to be zero.

CAPILLARY CONSTANTS AND SURFACE TENSIONS

Data obtained with Apparatus III (20.00°)

Radius of capillary = 1.0099 mm.

SUBSTANCE	AVERAGE HEIGHT IN MM.	CORRECTION FOR SMALL MENISCUS	CORRECTED HEIGHT IN MM.	DENSITY 20°/4°	CAPILLARY CONSTANT a ²	SURFACE TENSION DYNES PER MM ²
Water.....	14.394	0.321	14.715	0.99823	14.861	72.62
Benzene.....	6.351	0.311	6.662	0.8788	6.728	28.94
Toluene.....	6.369	0.311	6.680	0.8658	6.736	28.58

Data obtained with Apparatus IV (20.00°)

Radius of capillary = 0.1936 mm.

Benzene.....	34.620	0.061	34.681	0.8788	6.714	28.89
Methyl alcohol.....	30.063	0.061	30.124	0.7918	5.832	22.61
Ethyl alcohol.....	29.720	0.061	29.781	0.7892	5.766	22.27
Isobutyl alcohol....	30.016	0.061	30.077	0.8019	5.823	22.86
Ethyl butyrate.....	29.403	0.061	29.464	0.8789	5.704	24.53

It will be noted that, in general, these results are higher than most of the earlier results, for the reasons already suggested. For example, Quincke found only 14.47 as the capillary constant of water, and Renard and Guye found 6.47 for that of benzene. The carefully obtained results of Walden and Swinne, although measured in a fairly satisfactory apparatus, are all subject to the same error, because the apparatus was calibrated by means of a value of the capillary constant of benzene which is too low. It is hoped that an exact evaluation of the amount of this error may make it possible to correct the comprehensive and valu-

able work of Ramsay and Shields and Aston, as well as that of Renard and Guye, to the standard herewith shown to be more trustworthy.

This paper is only a preliminary communication. A fuller report of the work will appear in the July number of the *Journal of the American Chemical Society*. Much more work upon the subject has already been finished, and yet more is in prospect. We hope that yet further accuracy may be attained in the future, bearing in mind the precautions to which attention has been called in this paper, and that the results may be capable of fruitful discussion.

In conclusion, we are glad to express our indebtedness to the Carnegie Institution of Washington for some of the apparatus we have employed.

Summary.—In the course of a series of determinations of capillary constants by measuring the capillary rise in fine tubes, the following precautions have been especially emphasized: (1) The detection and correction of inequalities in the glass tubes employed were effected by the use of a reversible apparatus. (2) Reference of the capillary rise was made to an unrestricted flat surface 38 mm. in diameter, the largest ever used. It was shown that much smaller surfaces are too small and that the insertion of a capillary in the middle of a larger tube causes appreciable error by increasing the capillary effect of the large tube. (3) Especial care was taken that the true bottom of the meniscus should be read. (4) The weight of the fine meniscus was in each case allowed for, and a new approximate formula was suggested for its calculation, depending upon the observed height of the meniscus.

Heeding these precautions, determinations of the capillary constants of several important liquids were determined at 20° as follows: water 14.861, benzene 6.721, toluene 6.736, methyl alcohol 5.832, ethyl alcohol 5.793, isobutyl alcohol 5.823, ethyl butyrate 5.704.

AN EXHIBIT IN PHYSICAL ANTHROPOLOGY

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In the April number of the PROCEEDINGS OF THE NATIONAL ACADEMY OF SCIENCES, I published a brief account of "Some recent anthropological explorations," which were carried out under my direction or by myself, for the Smithsonian Institution and the Panama-California Exposition at San Diego, in different parts of the world. I shall now point, in an equally brief way, to the material results of these expeditions in relation with the Exposition.